The difference between Si and Ge(001) surfaces in the initial stages of growth

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The initial stages of growth of Ge and Si on the Ge(001) surface are studied and compared to growth on the Si(001) surface. Metastable rows of diluted ad-dimers exist on both surfaces as intermediate stages of epitaxial growth. Unexpectedly, for Ge(001) these rows are found exclusively in the $\langle 310 \rangle$ directions, whereas on Si(001) the preferred direction is $\langle 110 \rangle$. This qualitative difference between Si and Ge surfaces reflects the subtle difference in the chemistry of these two elements, which has direct consequences for epitaxial growth on these surfaces.

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The Si(001) surface is probably the most widely studied semiconductor substrate for understanding the processes which govern epitaxial growth, both experimentally and theoretically. Scanning tunneling microscopy (STM) has revealed a surprising richness of adsorbed structures even in the initial stages of homoepitaxial growth. In recent years growth of Si/Ge alloys and multilayers has received increased attention as such materials find new applications in semiconductor devices. For example, the controlled growth of these materials allows for band gap engineering in which, depending upon the composition, the band gap can be varied between that of Ge and Si. Growth on the Ge(001) surface has received much less attention than that on Si(001) which is surprising since in heterostructures both these surfaces play an equally important role. Probably this lack of attention reflects the general perception that one can derive the properties of the Ge surface from those of the Si surface because the chemistry of Si and Ge is very similar. Indeed Si and Ge(001) surfaces do have the same basic reconstruction and some of the structures formed by adsorbed species are very similar. As we will show in this paper, however, growth on Ge(001) does *not* necessarily follow the same pathway as on Si(001), despite the similarity in chemical bonding. In particular, the so-called "dilute" rows of ad-dimers, which form crucial intermediate structures in the growth process, have a different structure and dynamical behavior. This is caused by the difference in reactivity of the Ge and Si surfaces and it results in a much more ordered growth on the Ge surface.

Similar to Si(001), the basic reconstruction of the Ge(001) surface consists of surface atoms forming dimers which are arranged in rows. At room temperature, adsorbed single Si or Ge atoms are very mobile on the surface and the smallest structures observed are ad-dimers, i.e. bonded pairs of adatoms. Such ad-dimers play a prominent role in the low temperature growth of Ge and Si, and much work has been devoted recently to studying their energetics and their mobility [1, 2]. The basic (metastable) structures of ad-dimers are shown schematically in Fig. 1. Most of these dimer structures prove to be
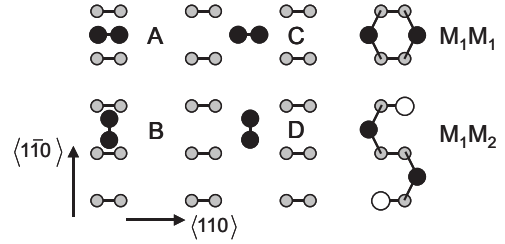

FIG. 1: Structures of Si or Ge ad-dimers and adatom pairs on Si or Ge(001) surfaces. Gray dumbbells represent substrate dimers, black circles the adsorbed atoms, and white circles the surface dangling bonds associated with the $M_1 M_2$ structure.

accessible kinetically and they can be observed in STM. From a population analysis one can, in principle, establish their relative energies. However, because of the kinetic barriers involved in the various diffusion processes, it can in practice be very difficult to achieve equilibrium on a surface.

It is also feasible to obtain such energy differences from first principles density functional calculations, simultaneously optimizing both the electronic structure and the geometry [3, 4]. The calculated total energy differences for Ge/Si ad-dimers on Ge/Si(001) surfaces are given in Table I. In detail the results depend somewhat upon the computational parameters used [3, 4, 6, 7, 8], but the overall trend is unambiguous. If one compares the numbers in Table I, one observes that the energy ordering is roughly the same in all cases. The B-type structure on-top of a substrate dimer row is lowest in energy. The "on-top" A and "in-between" C structures are somewhat higher in energy, the on-top position being slightly more favorable. The "in-between" D structure is substantially higher in energy, as are the adatom pairs $M_1 M_1$ and $M_1 M_2$. One would conclude that chemical bonding is the same for corresponding structures on the Ge(001) and Si(001) surfaces.

From the similarity of the energy landscapes sampled by diffusing species on these surfaces one would draw a similar conclusion. Diffusion barriers are quite hard

	Ge/Ge(001)	Si/Ge(001)	Ge/Si(001)	Si/Si(001)
A	0.18	0.24	0.06	0.01
C	0.23	0.26	0.19	0.28
D	0.80	0.63	1.01	0.95
$M_1 M_1$	0.48	0.76	0.27	0.39
$M_1 M_2$	0.65	0.93	0.53	0.71

TABLE I: Energies (eV) of the structures shown in Fig. 1 relative to the lowest energy structure, which is B in all cases.
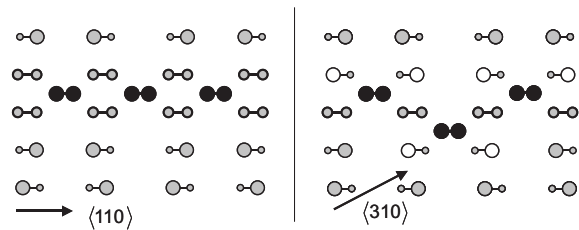

FIG. 2: Schematic representation of adsorbed $\langle 110 \rangle$ and $\langle 310 \rangle$ rows, as in Fig. 1. The size of the circles represents the height of the corresponding atoms.

to obtain from calculations, since one has to guess complete diffusion paths. Diffusion barriers are more easily obtained from STM experiments by timing the intervals between hopping events and extracting jump rates. For Ge ad-dimers on Ge(001), jump rates at room temperature have been measured for ad-dimers [9]. These can be translated into a diffusion barrier of 0.83 eV for diffusion of ad-dimers parallel to the substrate dimer rows (i.e. in the $\langle 1\bar{1}0 \rangle$ direction, cf. Fig. 1) and 0.95 eV for diffusion across the rows (in the $\langle 110 \rangle$ direction). The corresponding published numbers for diffusion of Si ad-dimers on the Si(001) surface are (in eV): 0.94 ± 0.09 [10] or 1.09 ± 0.05 [11] (parallel); 1.36 ± 0.06 [11] (across). The diffusion barriers on Ge(001) are lower, and the anisotropy of the diffusion is smaller. The former can be related to the lower cohesive energy of Ge as compared to Si, the latter can be explained by a subtle difference in surface structures. Whereas the bulk lattice constant of Ge is 4% larger than that of Si, the bond length of the surface dimers is 9% larger. It is then reasonable that the energy landscape for a diffusing ad-dimer on the Ge(001) surface is flatter, since the ad-dimer can more easily bridge the troughs between the substrate dimer rows. That the smaller anisotropy for diffusion can be attributed to the Ge(001) substrate rather than to the ad-dimer is confirmed by the diffusion barriers of a Si ad-dimer on the Ge(001) surface, which are 0.83 ± 0.05, and 1.0 eV for diffusion along and across the substrate dimer rows [12]. Skipping the quantitative differences, one notices that the relative order of the diffusion barriers in different directions is the same on both surfaces. This indicates a similar energy landscape for the diffusing species, at least with respect to the critical points of that landscape.

The theoretical and experimental evidence presented so far supports the suggestion that Ge(001) behaves similarly to Si(001); ad-dimers have similar structures and energies and their diffusion processes are similar. Since ad-dimers form the nuclei for growth on the surface, it is not unreasonable to suggest that growth on the Ge(001) and Si(001) surfaces proceeds via the same pathway. However, a distinct *difference* emerges in the next step. From STM studies of growth on the Si(001) surface, chain-like structures of ad-dimers in the $\langle 110 \rangle$ direction have been identified that are perpendicular to the substrate dimer

rows [13, 14, 15]. These are shown schematically in Fig. 2. They are observed both for Si on Si(001) as well as for Ge on Si(001) and are termed "dilute dimer rows". These are generally believed to play an important role as intermediate structures in the growth process [15].

On Ge(001) such dilute dimer rows are *not* observed at all, neither after deposition of Si nor of Ge. Instead the structures which are most frequently observed after low temperature deposition are rows of ad-dimers which are oriented in the [310] direction. Because of symmetry, ad-dimer rows in the [130] direction have the same energy, and "zigzag" rows which consist of [310] segments alternating with [130] segments occur very often, cf. Figs. 2 and 3. In the following we will use the phrase "$\langle 310 \rangle$ row" to label all such structures. $\langle 310 \rangle$ rows are also observed on Si(001), but gentle annealing of the surface seems to reduce their number in favor of the number of the dilute rows in the $\langle 110 \rangle$ direction. This would suggest that on Si(001) the $\langle 110 \rangle$ row is thermodynamically more stable, whereas the $\langle 310 \rangle$ row is easily accessible kinetically [14, 15]. On Ge(001) gentle annealing to 400 K renders the segments of a $\langle 310 \rangle$ row mobile, but a conversion into a $\langle 110 \rangle$ row is never observed [9].

As discussed above it is very difficult to achieve thermal equilibrium on a semiconductor surface. Moreover, annealing can only be done in a very gentle way, since increasing the temperature too much would destroy the absorbed "dilute" structures in favor of epitaxial islands. The stability of dilute dimer rows can be checked by first principles calculations. Table II gives the relative energies of dilute dimer rows of Si and Ge on Si(001) and Ge(001) substrates. Listed are the energy differences $E_{\langle 310 \rangle} - E_{\langle 110 \rangle}$ per adsorbed dimer between the $\langle 310 \rangle$ and $\langle 110 \rangle$ ad-dimer rows in the geometries shown in Fig. 2. The results are obtained for infinite rows which are compatible with the $p(4 \times 4)$ symmetry of the surface supercell used in the calculations [4]. The energy of a straight $\langle 310 \rangle$ row would probably be somewhat lower than that of the zigzag row consisting of alternating [310] and [130] segments shown in Fig. 2, and one would expect the energy of the latter to be an upper bound for "$\langle 310 \rangle$"-like rows. Even so, one can draw an unambiguous conclusion. On the Si(001) surface, $\langle 110 \rangle$ dilute ad-dimer rows

	Ge/Ge(001)	Si/Ge(001)	Ge/Si(001)	Si/Si(001)
ΔE(eV)	−0.12	−0.28	+0.28	+0.18

TABLE II: Energy difference $\Delta E = E\langle310\rangle - E\langle110\rangle$ per ad-dimer between rows of the geometries shown in Fig. 2

are lowest in energy by 0.2-0.3 eV/ad-dimer, whereas on Ge(001) the oblique or zigzag $\langle310\rangle$ rows are lowest in energy by 0.1-0.3 eV/ad-dimer. This conclusion holds both for Si and Ge ad-dimer rows, so the most stable structure seems to be dictated by the *surface* rather than by the *adsorbed species*.

In the following we will rationalize these results. The Si(001) and Ge(001) surface structures with lowest energy both have $c(4 \times 2)$ periodicity corresponding to the arrangement of buckled surface dimers shown schematically in Fig. 2. Adsorption of an ad-dimer row introduces a "domain wall" between two $c(4 \times 2)$ domains, which can be observed in Fig. 2 by noting that the substrate dimer rows beneath the adsorbed row are forced to be symmetric (non-buckled) [16]. This causes strain in the substrate. A $\langle310\rangle$ ad-dimer row introduces only one symmetric row in the substrate, whereas a $\langle110\rangle$ ad-dimer row introduces two such symmetric substrate rows. From the induced distortion of the surface geometry one would conclude that $\langle310\rangle$ ad-dimer rows are more favorable than $\langle110\rangle$ ad-dimer rows, since the former introduce fewer symmetric dimers and thus less strain in the substrate. On a clean surface, symmetric dimers are also found to be higher in energy than buckled dimers [17]. Moreover, the energy difference between symmetric and buckled surface dimers is larger on the Ge(001) surface than on the Si(001) surface [18]. Assuming this also holds for surface dimers underneath an adsorbed row, one would expect $\langle310\rangle$ ad-dimer rows on the Ge(001) surface to be relatively more stable.

We have not yet considered the chemical bonding between substrate and adsorbed dimers. A row of ad-dimers in the $\langle310\rangle$ structure leaves dangling bonds on the substrate. These are indicated in Fig. 2; simple electron counting would assign one electron per dangling bond. Being (partially) filled states with a high energy, such dangling bonds show up very prominently in a filled state STM image, cf. Fig. 3. In fact, they completely mask the adsorbed dimers in the filled state image. In contrast, a row of ad-dimers in the $\langle110\rangle$ structure leaves no such dangling bonds. On the basis of simple chemical reasoning one would expect the $\langle110\rangle$ ad-dimer rows to be more stable than the $\langle310\rangle$ ad-dimer rows, since the former leads to a smaller number of dangling bonds. Considering the two factors mentioned in this and the previous paragraph, the stability of the $\langle110\rangle$ versus $\langle310\rangle$ ad-dimer row structures results from a competition between the penalty for forming dangling bonds on the sub-
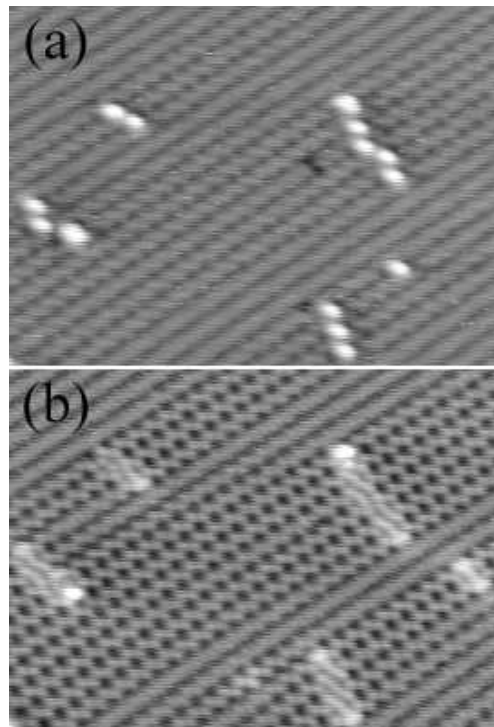

FIG. 3: STM images (size 13.5 nm x 17 nm) of a Ge(001)surface after the deposition of 0.02 ml Ge. (a) Empty state image; sample bias 1.6 V, tunneling current 0.7 nA. (b) Filled state image; sample bias −1.6 V, tunneling current 0.7 nA.

strate, which favors the former structure, and the penalty for forming symmetric substrate dimers, which favors the latter structure.

The Si(001) surface shows a strong tendency to minimize the number of dangling bonds on the substrate [19]. On a clean surface the surface dimers are bonded by π-bonds, as well as by σ-bonds. Adsorbed Si/Ge adatoms or single and "dilute" ad-dimers break these π-bonds but leave the σ-bonds intact. If only one atom of a substrate dimer is involved in the bonding to an adsorbed atom, the other atom of that dimer is left with a dangling bond, which is the remnant of the broken π-bond. One expects such a dangling bond to be higher in energy than a π-state and thus be more reactive. This is illustrated by the energy difference between the M_1M_2 and the M_1M_1 structures, Table I, which can roughly be interpreted as the penalty for creating two dangling bonds on the substrate, Fig. 1. This creation energy is 0.26-0.31 eV per pair of dangling bonds on a Si(001) surface, as compared to only 0.17 eV on a Ge(001) surface. Apparently π-bonding is stronger on Si(001) than on Ge(001) [20].

An adsorbed $\langle110\rangle$ row of ad-dimers only leaves dangling bonds on the surface at the end of a row, whereas a $\langle310\rangle$ row gives rise to two dangling surface bonds per adsorbed dimer. Chemical bonding thus favors adsorption in the $\langle110\rangle$ direction. On the basis of chemi-

cal bonding alone one would estimate the energy difference between the $\langle 310 \rangle$ and $\langle 110 \rangle$ rows on Si(001) to be $E(M_1 M_2) - E(M_1 M_1) \sim 0.3$ eV/ad-dimer in favor of the latter. The calculated energy differences of Table II for adsorbed rows on Si(001) are smaller, but not by much. This indicates that the strain induced by the $\langle 110 \rangle$ row is (at most) 0.1 eV/ad-dimer higher than that induced by the $\langle 310 \rangle$ row. A similar strain difference on the Ge(001) surface would already to a large part counteract the small energy difference between $\langle 310 \rangle$ and $\langle 110 \rangle$ adsorbed rows of < 0.2 eV/ad-dimer calculated on the basis of chemical bonding. In fact, from the calculated energy differences of Table II for adsorbed rows on Ge(001) one would conclude that the strain induced by the $\langle 110 \rangle$ row is $\gtrsim 0.3$ eV/ad-dimer higher than that induced by the $\langle 310 \rangle$ row. Note that this number compares very well with energy difference between symmetric and buckled dimers on the clean Ge(001) surface [18]. Energetically the strain difference on the Ge(001) surface tips the balance in favor of $\langle 310 \rangle$ adsorbed rows as compared to $\langle 110 \rangle$ rows.

We speculate that the difference in intermediate structures, $\langle 110 \rangle$ vs. $\langle 310 \rangle$, found on the Si(001) and Ge(001) surfaces has a substantial influence on the epitaxial growth on these surfaces. The effective binding energy between ad-dimers in a $\langle 110 \rangle$ row on the surface can be estimated by $E_{\text{bond}} = \frac{1}{2}(E_{\langle 110 \rangle} - 2E_{\text{dim}} + E_{\text{surf}})$, from the total energies $E_{\langle 110 \rangle}$ of the adsorbed row, E_{dim} of the adsorbed isolated dimer and E_{surf} of the clean surface, respectively. This estimate gives quite a high binding energy of $E_{\text{bond}} \sim 0.4$ eV for Si and Ge $\langle 110 \rangle$ ad-dimer rows on Si(001) while other rows have a binding energy of $E_{\text{bond}} \lesssim 0.2$ eV.

Several mechanisms have been proposed by which a $\langle 110 \rangle$ (dilute) ad-dimer row is transformed into an epitaxial structure. The density of dimers in an epitaxial row is twice as high as in a dilute row, so the transformation has to involve the incorporation of additional adatoms or dimers and/or the collapse of part of a dilute row into an epitaxial one [3, 14]. In any case the dilute $\langle 110 \rangle$ row acts as a growth nucleus and the epitaxial structure is also formed in the $\langle 110 \rangle$ direction. The transformation by insertion of adatoms/dimers can take place simultaneously at several positions in the dilute row. If these insertions take place in an uncorrelated way, this can easily lead to so-called "missing dimer" defects [21], i.e. epitaxial rows in which one or more dimers are missing. Such defects are quite common on the Si(001) surface and are extremely difficult to get rid off, even after careful annealing.

Ge ad-dimers in a $\langle 310 \rangle$ row on Ge(001) are much less strongly bound (the calculated effective binding energy is $E_{\text{bond}} \sim 0.1$ eV) and one expects such rows to break

up easily. Moreover, even in a $\langle 310 \rangle$ row the Ge ad-dimers are quite mobile [9]. Therefore we propose that the $\langle 310 \rangle$ row imposes less restriction on epitaxial growth on Ge(001) than does the $\langle 110 \rangle$ row on Si(001) and that it does not promote the formation of missing dimer defects. The result is that epitaxial growth on the Ge(001) surface can occur almost defect-free and that the Ge(001) surface contains far fewer defects than the Si(001) surface.

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